"Helium and Argon. Part III. Experiments which show the Inactivity of these Elements." By WILLIAM RAMSAY, Ph.D., F.R.S., and J. NORMAN COLLIE, Ph.D., F.R.S.E. Received April 22,—Read May 21, 1896.

To chronicle a list of failures is not an agreeable task; and yet it is sometimes necessary, in order that the record of the behaviour of newly discovered substances may be a complete one. It is with this object that we place on record an account of a number of experiments made to test the possibility of forming compounds of helium and argon.

It will be remembered that in our memoir on Argon,* Lord Rayleigh and Professor Ramsay described numerous experiments, made in the hope of inducing argon to combine, all of which yielded negative results. Two further experiments have been since made—again without success.

1. The electric arc was maintained for several hours in an atmosphere of argon. The electrodes were thin pencils of gas carbon, and, previous to the introduction of the argon, the arc was made in a vacuum, and all gas evolved was removed by pumping. Argon was then admitted up to a known pressure, and the arc was again made. A slow expansion took place; one of the electrodes diminished in length, and the bulb became coated with a black deposit. The resulting gas was treated with caustic soda and with a solution of ammoniacal cuprous chloride, and, on transference to a vacuum-tube, it showed the spectrum of argon along with a spectrum resembling that of hydrocarbons. Having to leave off work at this stage, a short note was sent to the 'Chemical News' on a Possible Compound of Argon. On resuming work after the holidays, the gas was again investigated, and, on sparking with oxygen, carbon dioxide was produced. But it was thought right again to treat the gas with cuprous chloride in presence of ammonia, and it now appeared that when left for a sufficient time in contact with a strong solution, considerable contraction took place, carbonic oxide being removed. There can, therefore, be no doubt that, although apparently all gas had been removed from the carbon electrodes before admitting argon, some carbon dioxide must have been still occluded, probably in the upper part of the electrodes, and that the prolonged heating due to the arc had expelled this gas and converted it into monoxide. It was, indeed, inexplicable how an expansion should have taken place unless by some such means; for the combination of a monatomic gas must necessarily be accompanied by contraction. It appears, therefore, certain that argon and carbon do not combine, even at

* 'Phil. Trans.,' vol. 186, A.

the high temperature of the arc, where any product would have a chance of escaping decomposition by removing itself from the source of heat. It is hardly necessary to point out that such a process lends itself to the formation of endothermic compounds such as acetylene, and it was to be supposed that if argon is capable of combination at all, the resulting compound must be produced by an endothermic reaction.

2. A product rich in barium cyanide was made by the action of producer gas on a mixture of barium carbonate and carbon at the intense temperature of the arc. This product was treated by Dumas' process so as to recover all nitrogen; and, as argon might also have entered into combination, the nitrogen was absorbed by sparking. All the nitrogen entered into combination with oxygen and soda, leaving no residue. Hence it may be concluded that no argon enters into combination. For the successful carrying out of these experiments we have to thank Mr. G. W. MacDonald.

3. A mixture of argon with the vapour of carbon tetrachloride was exposed for several hours to a silent discharge from a very powerful induction coil. The apparatus was connected with a gauge which registered the pressure of the vapour of the tetrachloride and of the argon of which it was mixed. Careful measurement of the pressure was made before commencing the experiment, and after its completion. Although a considerable amount of other chlorides of carbon was produced, no alteration of pressure was noticeable; the liberated chlorine having been absorbed by the mercury present. Here again the argon did not enter into the reaction, but it was recovered without loss of volume.

The remaining experiments relate to attempts to produce compounds of helium. The plan of operation was to circulate helium over the reagent at a bright red heat, and to observe whether any alteration in volume occurred—an absorption of a few c.c. could have been observed—or whether any marked change was produced in the reagent employed. As a rule, after the reagent had been allowed to cool in the gas, all helium was removed with the pump, and the reagent was again heated to redness, so as, if a compound had been formed, to decompose it and expel the helium. Every experiment gave negative results; in no case was there any reason to suspect that helium had entered into combination.

A short catalogue of the substances tried may be given.

4. Sodium distilled in the current of gas, and condensed in drops with bright metallic lustre. The glass tube in which it was heated became covered with a coating of

5. Silicon, which caused no absorption.

6. A mixture of beryllium oxide and magnesium, yielding metallic beryllium, was without action.

7. Zinc and, 8, cadmium distilled over in the current of gas.

9. A mixture of boron oxide and magnesium dust, giving elemental boron, produced no absorption.

10. Similarly, a mixture of yttrium oxide and magnesium dust had no effect.

11. Thallium was heated to bright redness in the gas, retaining its metallic lustre.

12. Titanium oxide mixed with magnesium dust was heated to bright redness, and caused no absorption.

13. Similar absence of action was proved with thorium oxide and magnesium powder.

14. Tin and, 15, lead, were heated to bright redness in the current of gas, and remained untarnished.

16. Phosphorus was distilled in the gas, and caused to pass through a length of combustion-tube heated to softening. Some red phosphorus was formed, but no alteration of volume was noticed.

17. The same process was repeated with elemental arsenic.

18. Antimony and, 19, bismuth, at a bright red heat, retained their metallic lustre.

20. Sulphur and, 21, selenium, were treated in the same way as phosphorus; no action took place.

22. Uranium oxide, mixed with magnesium dust, was heated to bright redness in helium. No change, except the reduction of the oxide, took place. The mixture was allowed to cool slowly in the current, and the helium was removed with the pump till a phosphorescent vacuum was produced in a vacuum tube communicating with the circuit. The mixture was re-heated, and no helium was evolved—not even enough to show a spectrum. The vacuum remained unimpaired.

It had been hoped that elements with high atomic weight, such as thallium, lead, bismuth, thorium, and uranium might have effected combination, but the hope was vain.

23. A mixture of helium with its own volume of chlorine was exposed to a silent discharge for several hours. The chlorine was contained in a reservoir, sealed on to the little apparatus which had the form of an ozone apparatus. No change in level of the sulphuric acid confining the chlorine was detected after the temperature, raised by the discharge, had again become the same as that of the room. Hence helium and chlorine do not combine.

24. Metallic cobalt in powder does not absorb helium at a red heat.

25. Platinum black does not occlude it.

26. It is not caused to combine by passage over a mixture of soda-lime and potassium nitrate heated to bright redness. This was hardly to be expected, for it resists the action of oxygen in presence of caustic soda, even when heated by the sparks which traverse it.

27. A mixture of soda-lime and sulphur consisting of polysulphides causes no change of volume in a current of helium passed over it at a bright red heat.

28. Induction sparks in an ozone apparatus passed through a mixture of helium with benzene vapour in presence of liquid benzene for many hours, gave no change of volume. The benzene was, of course, altered, but the sum of the pressures of the helium and the benzene-vapour remained as at first. Had helium been removed, contraction would have occurred.

This ends the catalogue of negative experiments. Any compound of helium capable of existence will probably be endothermic, and the two methods of producing endothermic compounds, where no simultaneous exothermic reaction is possible, are exposure to a high temperature, at which endothermic compounds show greater stability, and the influence of the silent electric discharge. These methods have been tried, so far in vain. There is, therefore, every reason to believe that the elements, helium and argon, are non-valent, that is, are incapable of forming compounds.

"On the Amount of Argon and Helium contained in the Gas from the Bath Springs."* By Lord Rayleigh, Sec. R.S. Received April 30,—Read May 21, 1896.

The presence of helium in the residue after removal of nitrogen from this gas was proved in a former paper,† but there was some doubt as to the relative proportions of argon and helium. A fresh sample, kindly collected by Dr. Richardson, has therefore been examined. Of this 2500 c.c., submitted to electric sparks in presence of oxygen, gave a final residue of 37 c.c., after removal of all gases known until recently. The spectrum of the residue, observed at atmospheric pressure, showed argon, and the D_3 line of helium very plainly.

The easy visibility of D_3 suggested the presence of helium in some such proportion as 10 per cent., and this conjecture has been confirmed by a determination of the refractivity of the mixture. It may be remembered that while the refractivity of argon approaches closely that of air, the relative number being 0·961, the refractivity of helium (as supplied to me by Professor Ramsay) is very low, being only 0·146 on the same scale. If we assume that any sample

* I am reminded by Mr. Whitaker that helium is appropriately associated with the Bath waters, which, according to some antiquaries, were called by the Romans *Aquæ Solis*.

† 'Roy. Soc. Proc.,' vol. 59, p. 206, 1896.